

# Rapid Screening of Metals Using Portable High-Resolution X-Ray Fluorescence Spectrometers

Alan D. Hewitt April 1995

#### **Abstract**

Analysis of copper, zinc, arsenic, lead, chromium, cobalt, nickel, mercury, thallium, selenium, silver, antimony, cadmium, tin, and barium was performed on soils and other particle matrices using two field-portable high-resolution X-ray fluorescence spectrometers (XRF). Quantitative determinations were based on fundamental parameter analysis and a second method that relies on analyte response factors and uses the Compton  $K_{\alpha}$  incoherent backscatter peak for matrix normalization. These two methods of instrumental analysis require only a few reference materials and are relatively insensitive to sample matrix composition. This study assessed the capability of these two rapid XRF analysis methods by determining metal concentrations in reference materials, field samples, and laboratory spiked soils. With the exception of nickel, cobalt, and chromium, concentrations within 50% of the expected values were consistently obtained at and below 1000  $\mu$ g/g.

For conversion of SI units to non-SI units of measurement consult ASTM Standard E380-93, *Standard Practice for Use of the International System of Units*, published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.

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Alan D. Hewitt April 1995

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#### **PREFACE**

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## Rapid Screening of Metals Using Portable High-Resolution X-Ray Fluorescence Spectrometers

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#### **INTRODUCTION**

Metal pollution over the past decade has come to be of greater concern due to an increasing awareness of the pathways leading to chronic human toxicity (Spittler and Fender 1979). During this time the use of X-ray fluorescence (XRF) analysis has increased for establishing the presence of elevated levels of metals in environmental samples (e.g., Furst et al. 1985, Piorek and Rhodes 1988, Grupp et al. 1989, Watson et al. 1989, Ashe et al. 1991, Carlson and Alexander 1991, Driscoll et al. 1991, Garby 1991, Harding 1991, Puls et al. 1994, etc.). This instrumental method of analysis establishes concentration estimates for several metals over a concentration range extending from percent levels to around  $100 \,\mu\text{g/g}$  (ppm). The method requires little or no sample pretreatment and can be performed for a small fraction of the time and cost associated with acid extraction/atomic absorption or emission analysis. Moreover, XRF analysis is nondestructive, so subsamples can be archived or analyzed by other procedures. For these reasons, XRF analysis is a very practical and economical method when screening for high concentrations of metals during a remedial investigation and feasibility study (RI/FS) at a suspected hazardous waste site.

Today several manufacturers offer energy-dispersive XRF spectrometers that have been designed to be compatible with field operations. The most transportable systems have a battery power supply option and use one or more radioactive sources as the primary incident radiation for elemental excitation. The first generation of these stand-alone systems was equipped with gas proportional detectors that had a spectral resolution on the order of 800–1000 electron volts (1000 eV = 1 keV). More recently, systems have been marketed (HNU Systems Inc., Spectrace Instru-

ments, Inc., Metorex, Inc.) with silicon (drifted with lithium) [Si(Li)] or mercuric iodide (HgI<sub>2</sub>) detectors capable of achieving resolutions of 170 and 300 eV, respectively. This increased spectral resolution allows for the unambiguous qualitative identification of metals in complex mixtures.

Quantitatively, however, the measurement of discrete spectral energies obtained by XRF analysis is often dependent on other metals present in the sample, due to absorption and enhancement effects. For environmental sample analysis, these matrix-specific effects are best addressed by the use of empirical coefficients (Piorek and Rhodes 1988). This method of instrumental calibration requires the acquisition or development of several well-characterized materials with a matrix composition similar to that of the samples. Moreover, the standards should contain a range of metal concentrations bracketing the desired level of quantitation. Due to these requirements, calibration standards are often both material and site specific, and their preparation and/or verification may take one or more weeks.

A more practical solution for an initial site investigation would be a calibration method that is insensitive to sample matrix so that only few standards would be needed to handle a diverse range of samples (e.g., soil composition "sand/slit/clay," sediment, sludge, dust, paint chips, etc.). Ideally, this capability would allow samples to be analyzed independent of any previous site characterization. With this concept in mind, two quantitation routines have been proposed for field-transportable high-resolution XRF systems. One routine is based on fundamental parameters (FP) analysis, which eliminates the need for several calibration standards by relying on certain physical constants to estimate metal concentration while theoretically correcting for matrix discrepancies (Figura 1987, 1993). Another approach uses response factors (RF) and corrects for matrix discrepancies by normalizing to the Compton  $K_{\alpha}$  (Comp.  $K_{\alpha}$ ) incoherent radiation backscatter peak.\*

This study evaluates these two methods of rapid sample analysis by determining the concentrations of copper (Cu), zinc (Zn), arsenic (As), lead (Pb), chromium (Cr), cobalt (Co), nickel (Ni), mercury (Hg), thallium (Tl), selenium (Se), silver (Ag), antimony (Sb), cadmium (Cd), tin (Sn), and barium (Ba) in a variety of solid-particle matrices. All analyses are performed with transportable high-resolution XRF systems that can be configured for stand-alone operations. This combination of rapid sample analysis and instrumental transportability is well suited for screening purposes, thus a data quality objective of an accuracy of  $\pm 50\%$  and detection limits of less than  $1000~\mu g/g$  was used (Raab et al. 1987).

#### INSTRUMENTATION

Explanations of the principals of XRF analysis can be found elsewhere (Driscoll et al. 1991, Hewitt 1994a, b). The instruments used in this study were the X-Met 920 (Metorex, Inc.; formerly Outokumpu Electronics) and the Spectrace 9000 (Spectrace Instruments) X-ray spectrophotometers. These two field-portable systems are equipped with surface analysis probes allowing for either in situ or intrusive sample analysis and have software-supported FP analysis capabilities. The Spectrace 9000 is equipped with three primary radioactive sources, Fe-55, Cd-109, and Am-241, and has a HgI<sub>2</sub> solidstate detector. The X-Met 920 has two radioactive sources, Cd-109 and Am-241, and has a Si(Li) detector that requires liquid  $N_2$  for operation. Table 1 lists some of the metals that can be determined by these XRF systems. The table also shows those metals that could be quantitated by FP software programs supplied by the respective manufacturers.

#### **CALIBRATION**

The FP software routines used in this study are proprietary to the instrument manufacturer. In general, these FP programs are a series of algorithms based on intensities measured for pure elements, sensitivity coefficients, summations of absorption-enhancement terms in appropriate matrices, and correction factors for overlapping peaks (Figura 1987). The X-Met 920 FP program also required the analysis of a fully characterized standard material, which for this study was SRM 2710, from the National Institute of Science and Technology (NIST).

To perform the RF/Comp.  $K_{\alpha}$  normalization analysis, a standard must be available that contains the analytes of interest in a matrix that is physically consistent (dry particles) with the samples. When possible, the RF should be established for well resolved  $K_{\alpha}$ ,  $K_{\beta}$ ,  $L_{\alpha}$ , or  $L_{\beta}$  spectral lines (Table 1). Figure 1 is an example of an XRF spectrum obtained with the X-Met 920 showing several characteristic peaks for metals along with the incoherent (Compton) and coherent (Rayleigh) sample matrix backscatter.

For this study a finely ground soil, SRM 2710 certified reference soil from NIST, was used to establish the analyte RFs for Cu, Zn, As, and Pb. Table 2 is an example of some of the daily RFs established for these four metals. For the determination of Cr, the NIST SRM 2711 was spiked with  $4000 \, \mu g$ 

Table 1. Primary sources and analyte lines for metals of environmental concern that can be detected by X-ray fluorescence spectrometry.

		Emission lines (keV)			
Source	Metals	$K_{\alpha}$	$K_{\beta}$	$L_{\alpha}$	$L_{oldsymbol{eta}}$
FE-55	Cr†	5.41	5.95		
Cd-109	Crt*	5.41	5.95		
Cd-109	Mnt	5.89	6.49		
Cd-109	Fet*	6.40	7.06		
Cd-109	Cot	6.92	7.65		
Cd-109	Nit	7.47	8.30		
Cd-109	Cu†*	8.04	8.94		
Cd-109	Znt*	8.63	9.61		
	Ast*	10.5	11.8		
Cd-109	Se†	11.2	12.6		
	Hg†			9.98	11.9
Cd-109	Tl			10.3	12.3
	Pb†*			10.5	12.6
Am-241	Agt	22.1	25.2		
Am-241	Cďt	23.1	26.4		
Am-241	Snt	25.2	28.8		
Am-241	Sb†	26.2	30.1		
Am-241	Bat	32.0	36.8		

Spectrace 9000 preprogrammed for fundamental parameter analysis of this metal.

<sup>\*</sup> T.M. Spittler, U.S. Environmental Protection Agency, Environmental Services Division, Region 1, Lexington, Massachusetts.

X-Met 920 preprogrammed for fundamental parameter analysis of this metal.

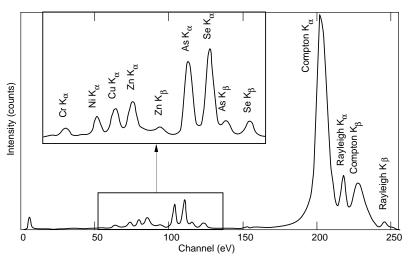


Figure 1. Spectrum of several characteristic  $K_{\alpha}$  and  $K_{\beta}$  peaks for metals and Compton and Rayleigh backscatter.

Table 2. Daily response factors established for Cu, Zn, As, and Pb based on the SRM 2710 certified reference material.

#### Response factor (intensity/concentration)

	Си	Zn	As	Pb
	12.0	33.9	1.09	39.5
	11.9	34.8	0.90	38.0
	12.3	34.4	1.04	39.6
Average	12.1	34.4	1.01	39.0
Std. dev.	0.21	0.45	0.098	0.90
% RSD	1.7	1.3	9.7	2.3
	SRM	2710 conce	entration (µ	1g/g)
	2950	6952	626	5532

Cr/g, to establish an RF. All of the other metals analyzed were quantified relative to RFs obtained for the Rocky Mountain Arsenal (RMA) soil matrix spiked with 1000 µg metal/g. Even with a high-resolution XRF instrument, the As  $K_{\alpha}$  and Pb  $L_{\alpha}$  lines (10.532 and 10.549 keV, respectively) overlap, so the As  $K_{\beta}$  and Pb  $L_{\beta}$  peaks were used. In addition, because high levels (>0.4%) of Fe were present in many of the laboratory-treated soil matrices, the Fe  $K_{\beta}$  peak (7.06 keV) had to be subtracted from the Co  $K_{\alpha}$  peak (6.92 keV), due to a spectral overlap. In the case of Co, the  $K_{\beta}$  line was not used because of insufficient response (intensity).

#### **ANALYSIS**

Only intrusive sample-analysis procedures were used in this study. Samples consisted of 2- to

5-gram quantities of air-dried materials with particle sizes averaging <600 µm in diameter. All samples were placed into 31-mm-diameter cups and covered with a 0.2-mil polypropylene X-ray film window. XRF analyses were performed for a period of 300 seconds. Field operations using these two preparation steps, i.e., drying and sieving, have shown that up to a hundred samples can be processed and analyzed within a single day (Grupp et al. 1989, Garby 1991).

Fundamental parameter sample analysis was performed using both XRF instruments after the selection of the appropriate software application and assessing

the instrumental tuning. For the Spectrace 9000 this involved checking the resolution and the background response with supplied reference materials and selecting the fine particle application. The FP software application supplied with the X-Met 920 system was based upon the analysis and total characterization of the finely ground NIST SRM 2710

The RF/Comp.  $K_{\alpha}$  normalization analysis method was only performed with the X-Met 920. To perform this method of analysis, the energy spectrum from each analysis was saved and transformed from a 2048- to a 256-channel spectrum for close examination. This approach was used because it was easier to measure the intensity of smoothed peaks and, once transformed, up to six spectra could be overlaid. Measurements included the intensity of elemental spectral lines and the intensity of the incoherent radiation backscatter peak (Comp.  $K_{\alpha}$ ). The intensity of the incoherent radiation backscatter reflects both the composition of light elements (e.g. carbon, nitrogen, silicon, etc.) in the sample matrix as well as the overall concentration of detectable analytes (Nielson and Sanders 1983). Intensities of both the baseline and peaks of interest were recorded from the computer display after selecting the appropriate spectrum channels. Concentration estimates were then manually determined by multiplying the baseline-corrected analyte signal intensity by the normalization factor, followed by the response factor. The normalization factor is the quotient of the Compton  $K_{\alpha}$ peak intensity of the certified reference material, divided by that of the samples. A more complete description of this analysis has been published elsewhere (Hewitt 1994a, 1994b).

#### **EXPERIMENTAL**

Several reference materials of different solid-waste matrices, along with field-contaminated and laboratory-treated soils, were analyzed to assess the performance of both the FP and RF/Comp.  $K_{\alpha}$  normalization.

#### Reference materials

Table 3 lists the certified reference materials purchased from NIST and the Resource Technology Corporation (RTC). Those purchased from NIST have certified concentrations for the total amount of metal present, whereas the RTC materials report certified values based on the USEPA SW846, 3000-series metal acid extraction procedures (U.S. EPA 1986).

#### Field samples

Six river sediment subsamples from a suspected hazardous-waste site were analyzed. These field subsamples were taken from thoroughly homogenized samples that had been previously characterized by inductively coupled plasma (ICP) analysis following 3000-series metal acid extraction procedures (U.S. EPA 1986).

#### Treated laboratory soils

Six different soils were spiked with Cr, Cu, Zn, As, Pb, Ni, Se, Hg, Tl, Co, Ag, Cd, Sn, Sb, and Ba by using concentrated 10,000 mg/L aqueous pure element atomic absorption standards (AESAR/

Table 3. List of certified reference materials.

SRM 1645—River sediment

SRM 1646—Estuarine sediment

SRM 1579a—Powdered lead-based paint

SRM 2704—Buffalo River sediment

SRM 2709—San Joaquin soil

SRM 2710-Montana soil

SRM 2711—Montana soil

Resource Technology Corporation

CRM012—Incinerated sludge

CRM014—Baghouse dust

CRM013—Paint chips

CRM020—Soil (from EPA Superfund site)

CRM021—Soil (from contaminated waste site)

Table 4. Characteristics of laboratory-treated soils.

	Sand	Silt and clay	Grain size*	Wt.†
Matrix	(%)	(%)	(µm)	(g)
Ottawa sand	100		400	4
Rocky Mountain Arsenal	NA	NA	NA	4
Lebanon landfill	45	55	300	4
CRREL soil	NA	NA	NA	4
Tampa Bay sediments	95	5	200	4
Ft. Edwards clay	30	70	30	2

- \* 95% cut off
- <sup>†</sup> Weight of soil subsample spiked

NA Not analyzed

Alfa, Johnson Matthey). A complete description of how these soil subsamples were treated has been presented elsewhere (Hewitt 1994b). The soil characteristics and the weight of the treated subsamples are shown in Table 4.

Briefly, the soils were air dried and thoroughly mixed prior to placing subsamples into 31-mmdiameter analysis cups. Analyte spikes were made by pipetting between 0.4 and 0.025 mL quantities of the aqueous standards directly onto the individual soil subsamples, increasing the metal concentration by 1000, 500, 250, 125, or  $0 \mu g/g$ . Only five analytes were applied to a set of five replicate soil subsamples in order to limit the total volume of solution added to each subsample (0.2 mL/g). Following this protocol, one set of 30 soil subsamples  $(5 \times 6)$  was spiked with Cr, Cu, Zn, As, and Pb, a second with Ni, Se, Hg, Tl, and Co, and a third with Ag, Cd, Sn, Sb, and Ba. Analyte additions were performed so that a given soil subsample was not treated with the same concentration more than once (Table 5). A sixth untreated subsample of each soil type was also analyzed with each group and served as the matrix blank.

#### **RESULTS AND DISCUSSION**

Table 6 lists the estimates of detection reported by the manufacturers for FP analysis, along with some values established using the RF/Comp.  $K_{\alpha}$  normalization and method detection limit (MDL) (Federal Register 1984). This table also includes the analyte intensities measured for the RMA soil treated with 1000 µg metal/g. These intensities were included to provide a means of predicting a detection limit, based on the assumption that there is a fairly constant inverse relationship between these two parameters. This table indicates that regardless of the method of analysis, all of these

Table 5. Treatment scheme for spiking soil subsamples with metals.

Sets	Metal groups							
1	Cr	Cu	Zn	As	Pb			
2 3	Ni Sb	Se Ag	Hg Ba	Tl Cd	Co Sn			
	Treatment concentrations							
Subsam	ple							
S1	1000*	125	0	500	250			
S2	500	250	1000	0	125			
S3	250	0	125	1000	500			
S4	125	1000	500	250	0			
S5	0	500	250	125	1000			
Matrix								
blank	NF	NF	NF	NF	NF			

<sup>\*</sup> μg/g NF Not fortified

Table 6. Detection limit estimates and intensity counts.

	Detection limits (μg/g)					
		Spectrace	X-Met	RF/	Peak	
Source	Metal	9000*	920 <sup>†</sup>	Compt.**	intensity*†	
FE-55	Cr	180	_	_	_	
Cd-109	Cr	525	325	270	1.18	
Cd-109	Mn	410	225	_	_	
Cd-109	Fe	225	200	_	_	
Cd-109	Co	205	180	_	1.33	
Cd-109	Ni	125	175	_	3.82	
Cd-109	Cu	90	175	54	6.58	
Cd-109	Zn	70	160	90	6.47	
Cd-109	As	50	140	42	3.18	
Cd-109	Se	35	140	_	18.0	
Cd-109	Hg	60	_	_	5.33	
Cd-109	T1	_	_	_	7.83	
Cd-109	Pb	30	_	48	8.34	
Am-241	Ag	_	70	_	25.9	
Am-241	Cď	180	100	_	24.6	
Am-241	Sn	100	80	_	27.1	
Am-241	Sb	65	80	_	33.5	
Am-241	Ва	20	100		31.4	

- \* Minimum detection limit
- <sup>†</sup> Minimum determination limit
- \*\* Method detection limit

metals should be easily quantitated below 1000  $\mu g/g$  by XRF analysis.

Tables 7 and 8 show the concentration estimates obtained for the commercial reference materials by these two methods of rapid sample analysis. These two tables show results for Cu, Zn, As, and

Pb when the certified concentration was above one of the estimates of detection listed in Table 6. In only two cases were the values established by the RF/Comp.  $K_{\alpha}$  normalization method off by more than ±50% from the certified values. An apparently high concentration was established for Cu in the CRM 021 soil, and a low one for the SRM 2704 river sediment. Fundamental parameter analysis with the Spectrace 9000 XRF failed to establish concentrations within ±50% six times, twice each for Cu, As, and Pb. No values were obtained for Cu in the SRM 2704 river sediment and SRM 2711 soil, while low determinations of As occurred for both the SRM 2710 soil and the CRM 020 soil, and high estimates were obtained for Pb in the CRM 013 paint chips and the CRM 014 baghouse dust. The FP determinations made with the X-Met 920 failed to meet this criterion in only three cases. Alow value was established for As in the CRM 020 and high values for Pb in both the CRM 013 paint chips and the CRM 014 baghouse dust.

The high values obtained for the CRM reference materials by these two methods of XRF analysis are not necessarily incorrect, since the certified value is based on an acid extraction that does not necessarily represent the total amount present. However, a low determination for these standards, or one that fails to be within ±50% of the value stated for the NIST reference materials, would be aberrant. The low As concentrations determined by FP analysis had previously been identified as a problem when samples contain much larger (>10 times) quantities of Pb (Harding 1991). The falsenegative Cu determinations were only for samples with certified concentrations very close to the estimates of detection. Overall, these two rapid methods of analysis showed that they were fairly insensitive to this wide variety of particulate matrices by establishing concentrations that would be appropriate for the data quality objectives stated.

Table 9 shows XRF concentration estimates obtained for Cu, Zn, and Pb along with the values obtained by acid-extraction/ICP analysis. The FP analysis was only performed with the X-Met 920 XRF analyzer. In those cases where the values obtained by acid-extraction/ICP analysis were above the appropriate estimate of detection (Table 6), only Cu in sample A and Zn in sample F had XRF estimates that were off by more than  $\pm 50\%$ . A high Cu value was established by RF/Comp.  $K_{\alpha}$  normalization analysis, and a high Zn value was established by FP analysis. Again, since these reported estimates were higher than those obtained after acid extraction and ICP analysis, which is not nec-

<sup>\*†</sup> Matrix-corrected peak intensity for 1000-ppm spiked RMA soil

essarily a total concentration, the XRF values may not be incorrect.

The concentration estimates for Cu, Zn, As, Pb, Cr, Co, Ni, Hg, Tl, Se, Ag, Cd, Sn, Sb, and Ba in the laboratory-spiked soil subsamples appear in Tables 10 through 15. Tables 10–12 show the values for RF/Comp.  $K_{\alpha}$  normalization analysis, and Tables 13–15 show the values for FP analysis using the Spectrace 9000 XRF analyzer. In addition to these metals that were spiked onto the soils, values for iron (Fe) determined by FP analysis are reported in Table 14. Thallium was not determined by FP analysis because this metal had not been included in the software program. All of these concentration estimates were established by using either Cd-109 or Am-241 incident radiation (Table 1).

The values in these tables were corrected for

Table 7. Analysis of commercial reference materials from the National Institute of Standards and Technology.

	Metal concentrations (μg/g)				
Standard	Си	Zn	As	Pb	
SRM 1645 river sediment	109** [72]	1720** [1900]		714** [638]	
	114*	1760*		606*	
SRM 1646		138**			
estuarine sedimen	t	[127]			
SRM 1579a lead-based paint				119,950** [160,000] 144,000 <sup>†</sup> 124,000*	
SRM 2704 river sediment	99** [31] ND <sup>†</sup>	438** [302] 464 <sup>†</sup> 527*		161** [130] 133 <sup>†</sup> 200*	
SRM 2709 soil		106** [91] 129 <sup>†</sup>			
SRM 2710 soil	2950** 3350 <sup>†</sup>	6952** 7570 <sup>†</sup>	626** 149 <sup>†</sup>	5532** 6240 <sup>†</sup>	
SRM 2711 soil	114** [167] ND <sup>†</sup>	350** [343] 410 <sup>†</sup> 414*	105** [138] ND <sup>†</sup>	1162** [1100] 1280 <sup>†</sup> 1210*	

<sup>\*\*</sup> Certified concentration

ND Not detected

background concentrations present in the soil matrix and for spectral overlap interferences. These corrections were made when both the subsample in the treatment set (Table 5) with no spiked analyte and the subsample of the untreated matrix were determined to have concentrations that exceeded the respective estimates of detection listed in Table 6. However, in cases where there was no estimate of detection for the RF/Comp.  $K_{\alpha}$  normalization method of analysis, the lowest value appearing in this table was used. Corrections for Cu, Zn, and Ba were necessary because these metals were present at detectable levels in some of the soil matrices. Corrections were required for Co because of a spectral overlap with the  $K_{\beta}$  peak of Fe and for Ag due to spectral overlap with a peak characteristic of the Am-241 primary radiation source.

Table 8. Analysis of commercial reference materials from the Resource Technology Corporation.

	Metal concentrations ( $\mu g/g$ )				
Standard	Си	Zn	As	Pb	
CRM012	3015**	635**		120**	
incinerated	[2470]	[342]		[114]	
sludge	3590 <sup>†</sup>	744 <sup>†</sup>		126 <sup>†</sup>	
<i>G</i> -	3340*	525*		60*	
CRM 013				643**	
paint chips				[460]	
1 1				2160 <sup>†</sup>	
				998*	
CRM 014				1914*	
baghouse dust				[2080]	
O				5360t	
				4925*	
CRM 020 soil	753**	3021**	397**	5195**	
	[687]	[4420]	[429]	[5070]	
	521 <sup>†</sup>	3550 <sup>†</sup>	113 <sup>†</sup>	4580 <sup>†</sup>	
	684*	3898*	126*	4950*	
CRM 021 soil	5086**	574**			
	[8720]	[549]			
	3060 <sup>†</sup>	408 <sup>†</sup>			

<sup>\*\*</sup> Certified concentration

<sup>[]</sup> Concentration estimate based on response factor/Compton  $K_{\alpha}$  peak normalization with X-Met 920

<sup>&</sup>lt;sup>†</sup> Concentration estimate based on fundamental parameter analysis with Spectrace 9000

Concentration estimate based on fundamental parameter analysis with X-Met 920

<sup>[]</sup> Concentration estimate based on response factor/ Compton  $K_{\alpha}$  peak normalization with X-Met 920

<sup>†</sup> Concentration estimate based on fundamental parameter analysis with Spectrace 9000

<sup>\*</sup> Concentration estimate based on fundamental parameter analysis with X-Met 920

ND Not detected

Table 9. Concentrations ( $\mu$ g/g) of Cu, Zn, and Pb determined for field soil samples.

	Metal concentrations (μg/g)				
Field samples	Си	Zn	Pb		
A	114**	1140**	253**		
	[176]	[1260]	[229]		
	286*	1500*	318*		
В	776**	1390**	488**		
	[756]	[1310]	[473]		
	984*	1810*	614*		
С	1860**	261**	2060**		
	[1750]	[182]	[1650]		
	1600*	220*	1600*		
D	3960**	735**	546**		
	[3270]	[408]	[475]		
	3510*	688*	494*		
Е	449**	1260**	350**		
	[443]	[1230]	[328]		
	567*	1710*	416*		
F	104**	182**	87**		
	[145]	[200]	[108]		
	331*	391*	245*		

- \*\* Concentrations based on acid-extraction/ ICP analysis
- [] Concentration estimate based on response factor/Compton  $K_{\alpha}$  peak normalization with X-Met 920
- Concentration estimate based on fundamental parameter analysis with X-Met 920

This study of laboratory-spiked soils was included because commercial reference materials typically contain only a few metals (e.g., Cu, Zn, Pb) at concentrations that can be readily detected by XRF analysis. The soil spiking method used (Hewitt 1994b) appears to have resulted in fairly homogenous and accurate analyte concentrations, as shown by Figures 2 and 3. Plots of the results of Pb and Sb were chosen to show this feature because XRF analysis is particularly sensitive for these two metals (Table 6), and they are representative of metals excited by the Cd-109 and Am-241 primary sources, respectively. It is logical to assume that the other metals spiked onto the different soil matrices were likewise evenly distributed.

The results in Tables 10–15 show that these two methods of rapid sample analysis consistently established concentrations for Cu, Zn, Pb, Se, Ag, Sn, Sb, and Ba that were within  $\pm 50\%$  of the expected values from 1000 to 125 ppm. This was also the case for Hg as determined by RF/Comp.  $K_{\alpha}$  normalization analysis. The few aberrant values for Hg, as established by FP analysis with the

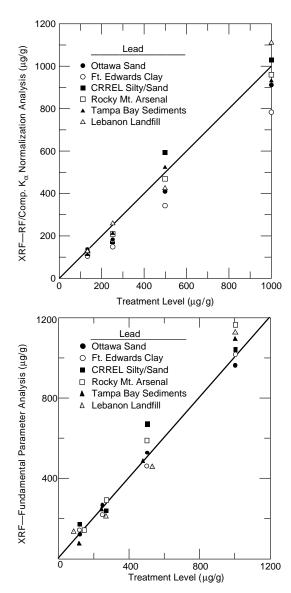


Figure 2. Lead concentrations ( $\mu g/g$ ) established for spiked soils by both RF/Comp.  $K_{\alpha}$  normalization and FP analysis.

Spectrace 9000, were most likely caused by a peak overlap with Tl. This problem occurred because Tl had not been one of the metals included in the FP software. With the exception of a few values established for the two lowest treatment levels for As and Cd (and Tl by RF/Comp.  $K_{\alpha}$ ) these metals were also within the  $\pm 50\%$  concentration criterion. Clearly, the concentrations of all of these metals can be adequately estimated at  $1000~\mu g/g$  and below by these two rapid methods of XRF analysis. Furthermore, since both methods established concentration trends that were consistent with the treatment levels, they would correctly define the areas of greatest concern.

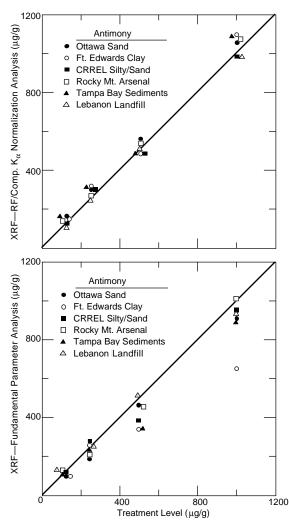


Figure 3. Antimony concentrations ( $\mu g/g$ ) established for spiked soils by both RF/Comp.  $K_{\alpha}$  normalization and FP analysis.

The remaining metals in this study, Ni, Co, and Cr, required additional qualifications because their estimates of detection precluded some of the lower laboratory treatment levels. For instance, Ni and Co could only be assessed for spiked concentrations that were >205 ppm  $(\mu g/g)$ , likewise Cr for concentrations >525 ppm and >270 ppm for FP and the RF/Comp.  $K_{\alpha}$ analysis, respectively. Values for all three of these metals were established by both methods of analysis that failed to meet the ±50% concentration criterion. High concentration estimates tended to be established for both Ni and Co by FP analysis in soils with low Fe content (Table 14). In contrast, low concentrations of these two metals were established by RF/Comp.  $K_{\alpha}$  normalization analysis when high levels of Fe were present. Both meth-

Table 10. Concentrations ( $\mu$ g/g) of Cr, Cu, Zn, As, and Pb determined for spiked soil matrices by response factor/ Compton  $K_{\alpha}$  peak normalization.

	Metal concentrations (μg/g)				
Material & spike	Си	Zn	As	Pb	Cr
Ottawa sand					
1000 ppm	1010*	1020	1420	911	1770
500 ppm	534*	458	381	411	856
250 ppm	264*	224	324	182	312
125 ppm	132*	127	72	139	84
0 ppm	69	ND	ND	ND	ND
Matrix	64	18	ND	10	ND
Ft. Edwards clay					
1000 ppm	711*	751*	906	785	979
500 ppm	289*	374*	491	344	638
250 ppm	144*	252*	229	150	175
125 ppm	142*	91*	104	108	304
0 ppm	199	81	ND	19	46
Matrix	218	80	ND	4	ND
CRREL soil					
1000 ppm	787*	870	782	1030	1100
500 ppm	461*	541	635	597	439
250 ppm	250*	247	320	178	220
125 ppm	69*	152	26	130	250
0 ppm	86	48	48	ND	93
Matrix	62	59	ND	18	257
Rocky Mountain Arsenal	l				
1000 ppm	897*	1050	1450	960	1160
500 ppm	483*	459	608	470	493
250 ppm	209*	245	304	211	349
125 ppm	93*	153	105	125	229
0 ppm	76	ND	37	ND	205
Matrix	62	2	41	23	ND
Tampa Bay sediments					
1000 ppm	842*	939	1350*	936	1570
500 ppm	513*	486	560*	526	653
250 ppm	250*	218	200*	219	639
125 ppm	103*	159	73*	124	219
0 ppm	60	11	220	7	120
Matrix	71	ND	249	ND	99
Lebanon landfill soil					
1000 ppm	859*	872	988	1192	1500
500 ppm	373*	469	536	423	495
250 ppm	195*	224	305	264	407
125 ppm	94*	140	78	135	326
0 ppm	99	2	ND	ND	ND
Matrix	70	8	ND	24	ND

<sup>\*</sup> Average of 0 ppm and matrix subsamples subtracted

ods of analysis tended to establish high estimates for Cr for soil matrices with low Fe content. Even though this apparent matrix effect was not adequately handled by either of these two methods of analysis to meet the  $\pm 50\%$  criterion consistently, the appropriate concentration trends were established.

Table 11. Concentrations ( $\mu$ g/g) of Co, Ni, Hg, Tl, and Se determined for spiked soil matrices by response factor/ Compton  $K_{\alpha}$  peak normalization.

Metal concentrations (μg/g) Material & spike CoNi Hg Se Ottawa sand 758 909 977 1000 ppm 1250 1230 532 471 502 500 ppm 539 609 250 ppm 267 290 149 421 231 199 90 132 225 125 ppm 89 0 ppm ND ND 13 52 ND 13 ND ND Matrix ND ND Ft. Edwards clay 200\* 1000 ppm 496 623 813 675 500 ppm 482 50\* 260 268 449 250 ppm ND\* 187 145 347 136 ND\* 199 125 ppm 90 120 73 0 ppm 6500 45 ND 63 ND Matrix 6300 16 ND ND ND CRREL soil 1000 ppm 390\* 761 823 993 882 ND\* 500 ppm 356 323 553 519 250 ppm 180\* 93 141 330 238 125 ppm ND\* 15 225 128 110 0 ppm 4050 ND 43 66 8 4070 ND ND ND Matrix ND Rocky Mountain Arsenal 560\* 947 933 1030 977 1000 ppm 500 ppm 270\* 481 395 545 483 250 ppm 60\* 298 179 449 211

50\*

1580

1680

846\*

482\*

178\*

103\*

193

135

435\*

395\*

135\*

85\*

2260

2170

125 ppm

0 ppm

Matrix

500 ppm

250 ppm

125 ppm

1000 ppm

500 ppm 250 ppm

125 ppm

0 ppm

Matrix

0 ppm

Matrix

Tampa Bay sediments 1000 ppm

Lebanon landfill soil

86

12

ND

962

457

315

129

22

ND

838

470

179

88

ND

ND

161

21

ND

933

395

179

161

21

ND

550

472

207

148

21

ND

216

33

12

997

519

425

199

73

7

996

460

435

253

45

14

111

ND

ND

1010

460

221

124

ND

11

968

511

192

123

ND

ND

\* Average of 0 ppm and matrix subsamples subtracted

Several factors that control the sensitivity of elemental analysis by XRF analysis are independent of matrix composition. First of all, elements with low atomic numbers have low fluorescence yields (Fig. 4). The fluorescence yield is the ratio of number of vacancies created within an atom by the incident radiation to the number of vacancies that

Table 12. Concentrations ( $\mu g/g$ ) of Ag, Cd, Sn, Sb, and Ba determined for spiked soil matrices by response factor/Compton  $K_{\alpha}$  peak normalization.

	Metal concentrations ( $\mu g/g$ )					
Material & spike	Ag	Cd	Sn	Sb	Ва	
Ottawa sand						
1000 ppm	1170	1000	986	1060	1160	
500 ppm	646	499	398	557	527	
250 ppm	269	176	226	302	262	
125 ppm	109	48	145	160	121	
0 ppm	19	ND	97	ND	ND	
Matrix	25	ND	25	12	NE	
Ft. Edwards clay						
1000 ppm	1032*	936	899	1080	996	
500 ppm	604*	334	447	495	496	
250 ppm	297*	162	248	317	288	
125 ppm	166*	42	146	152	163	
0 ppm	312	ND	92	ND	703	
Matrix	263	ND	26	20	665	
CRREL soil 1000 ppm	896*	1040	918	996	1030	
500 ppm	363*	531	459	493	489	
250 ppm	179*	253	286	295	273	
125 ppm	82*	153	142	142	118	
0 ppm	169	ND	81	ND	392	
Matrix	159	ND	36	14	410	
Rocky Mountain Arsen						
1000 ppm	992*	984	745	1070	1060	
500 ppm	410*	416	418	538	530	
250 ppm	297*	142	246	274	220	
125 ppm	140*	42	155	143	130	
0 ppm	246	ND	95	ND	914	
Matrix	230	ND	37	11	967	
Tampa Bay sediments						
1000 ppm	1210*	1060	899	1080	1050	
500 ppm	567*	488	447	495	596	
250 ppm	368*	203	348	317	287	
125 ppm	153*	94	146	152	152	
0 ppm	167	ND	92	ND	28	
Matrix	160	ND	26	20	29	
Lebanon landfill soil						
1000 ppm	1040	1070	902	1060	990	
500 ppm	535	436	454	496	498	
250 ppm	314	297	248	304	247	
125 ppm	180	182	150	144	118	
0 ppm	49	36	90	ND	360	
Matrix	55	72	31	15	439	

<sup>\*</sup> Average of 0 ppm and matrix subsamples subtracted

actually result in the production of characteristic X-ray photons (Jenkins 1986). In addition, since only a few isotopes are available for field-portable XRF systems, there can be a large separation between incident and excitation energies. The greater this separation, the lower the analyte response, because fewer atoms become excited. A third factor

Table 13. Concentrations ( $\mu g/g$ ) of Cr, Cu, Zn, As, and Pb determined by fundamental parameter analysis using the Spectrace 9000.

Metal concentrations ( $\mu g/g$ ) Material & spike Си Zn AsPbCr Ottawa sand 1000 ppm 1430 1320 1380 976 3010 500 ppm 731 652 389 531 1120 270 287 335 274 250 ppm 580 102 152 51 131 310 125 ppm ND ND ND ND ND 0 ppm Matrix ND ND ND ND 10 Ft. Edwards clay 1000 ppm 1340 1140\* 1020 1020 850 532 524\* 467 300 500 ppm 660 250 ppm 334 192\* 343 225 ND 125 ppm 227 147\* 13 138 ND 99 0 ppm 131 ND ND ND Matrix 67 99 ND ND 66 CRREL soil 1000 ppm 1130 1270\* 1280 1040 940 500 ppm 489 550\* 656 657 57 250 ppm 253 221\* 311 232 53 125 ppm 77 120\* 60 172 ND ND 74 ND 0 ppm ND ND Matrix ND 95 56 ND ND Rocky Mountain Arsenal 1350 1170 1480 1000 ppm 1280 1240 500 ppm 678 675 636 589 440 250 ppm 236 333 375 281 280 125 ppm 74 125 19 141 120 0 ppm ND ND 22 ND ND Matrix ND 36 28 ND ND Tampa Bay sediments 1000 ppm 1210 1250 1230 1100 1490 500 ppm 662 545 651 477 700 250 ppm 312 289 278 256 120 83 125 ppm 70 118 63 ND ND ND 12 ND 0 ppm 66 Matrix ND ND 23 ND ND Lebanon landfill soil 1000 ppm 1130 1130 1110 1130 1350 500 ppm 584 613 567 460 450 316 332 250 ppm 327 218 150 125 ppm 71 133 59 130 ND 0 ppm ND 13 11 ND ND

ND

22

43

ND

ND

Matrix

is the depth of penetration achieved by the incident radiation, i.e., how much of the sample is actually analyzed. The penetration depth of incident radiation is inversely proportional to its wavelength and directly proportional to its energy. For the sources used in this study, the depth of penetration (99% attenuation) for a quartz matrix

Table 14. Concentrations ( $\mu g/g$ ) of Co, Ni, Hg, Se, and Fe determined by fundamental parameter analysis using the Spectrace 9000.

	Metal concentrations (μg/g)					
Material & spike	Со	Ni	Hg	Se	Fe	
Ottawa sand						
1000 ppm	1830	1538	1010	1240	NI	
500 ppm	994	846	781	637	7	
250 ppm	442	427	228	307	6	
125 ppm	109	183	380	143	12	
0 ppm	ND	ND	111	ND	11	
Matrix	ND	ND	ND	ND	142	
Ft. Edwards clay						
1000 ppm	727*	999	791	1100	55,40	
500 ppm	277*	495	458	503	54,60	
250 ppm	67*	207	200	265	56,70	
125 ppm	ND*	12	360	120	57,00	
0 ppm	560	ND	80	ND	55,60	
Matrix	406	ND	ND	ND	56,90	
CRREL soil						
1000 ppm	965*	1210	1321	1350	40,00	
500 ppm	295*	624	665	611	40,90	
250 ppm	235*	216	259	332	41,10	
125 ppm	315*	148	155	146	41,10	
0 ppm	190	11	95	ND	41,30	
Matrix	280	ND	16	ND	40,90	
Rocky Mountain Arsen	al					
1000 ppm	1490	1480	1170	1390	18,60	
500 ppm	900	786	736	689	19,60	
250 ppm	479	324	301	304	22,50	
125 ppm	224	141	579	140	21,70	
0 ppm	ND	ND	121	ND	21,10	
Matrix	ND	ND	ND	ND	20,10	
Tampa Bay sediments						
1000 ppm	1710	1720	1350	1310	441	
500 ppm	738	687	728	758	424	
250 ppm	423	308	356	350	393	
125 ppm	198	152	529	185	347	
0 ppm	122	32	151	ND	350	
Matrix	24	ND	ND	ND	419	
Lebanon landfill soil						
1000 ppm	1330	1280	1040	1260	24,90	
500 ppm	660	578	744	705	25,90	
250 ppm	208	294	227	346	25,50	
125 ppm	160	119	336	134	27,20	
0 ppm	ND	ND	151	ND	25,60	
Matrix	109	14	ND	ND	25,70	

<sup>\*</sup> Average of 0 ppm and matrix subsamples subtracted

ranges from 40 mm for Am-241 to 4.8 mm for Cd-109. The combination of these factors controls the intensity that will be measured for a given element. For example, Table 6 shows the range of analyte intensities obtained for the same concentration in the RMA soil.

To illustrate the combination of these two ef-

<sup>\*</sup> Average of 0 ppm and matrix subsamples subtracted

Table 15. Concentrations ( $\mu$ g/g) of Ag, Cd, Sn, Sb, and Ba determined by fundamental parameter analysis using the Spectrace 9000.

	Metal concentrations (μg/g)					
Material & spike	Ag	Cd	Sn	Sb	Ва	
Ottawa sand						
1000 ppm	937	1110	1000	915	772	
500 ppm	504	581	429	474	353	
250 ppm	274	394	269	196	174	
125 ppm	193	229	174	109	75	
0 ppm	77	111	43	ND	ND	
Matrix	25	74	41	ND	ND	
Ft. Edwards clay						
1000 ppm	820	976	857	654	601*	
500 ppm	377	542	452	345	300*	
250 ppm	197	361	226	261	215*	
125 ppm	86	172	154	108	148*	
0 ppm	ND	127	74	ND	379	
Matrix	ND	100	81	17	436	
CRREL soil						
1000 ppm	998	1060	1050	955	715*	
500 ppm	508	584	527	490	381*	
250 ppm	268	302	301	276	201*	
125 ppm	191	225	153	122	92*	
0 ppm	67	51	37	16	288	
Matrix	40	99	28	ND	329	
Rocky Mountain Arsena	al					
1000 ppm	1060	1200	1040	1010	850*	
500 ppm	535	613	486	562	472*	
250 ppm	296	406	336	221	250*	
125 ppm	190	253	194	133	105*	
0 ppm	77	143	33	22	716	
Matrix	37	80	58	14	734	
Tampa Bay sediments						
1000 ppm	989	1141	1030	897	706	
500 ppm	486	557	485	445	365	
250 ppm	268	299	205	235	215	
125 ppm	181	189	114	115	92	
0 ppm	56	42	51	ND	ND	
Matrix	56	84	55	12	ND	
Lebanon landfill soil						
1000 ppm	914	1190	1020	930	832*	
500 ppm	525	608	538	515	343*	
250 ppm	301	337	287	259	232*	
125 ppm	205	223	165	133	111*	
0 ppm	39	66	41	ND	278	
Matrix	ND	18	71	18	300	

<sup>\*</sup> Average of 0 ppm and matrix subsamples subtracted

fects, matrix composition and characteristic analyte response, Figure 5 shows the average concentration and standard deviations for the  $1000\,\mu g$  metal/g spiked soil matrices. Overall, both the precision and accuracy of analysis improves with atomic number. However, for Cr, Co, and Ni, the degree of bias and range of uncertainty shows that values

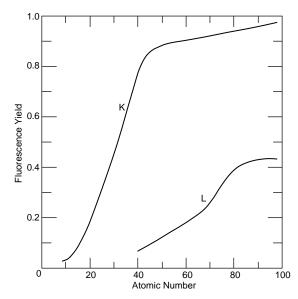


Figure 4. Fluorescence yield vs. atomic number for K and L lines.

even at this level can be greater than ±50% from the true concentration when analyzing a variety of soils. Most likely, the bias in the determined concentrations is the result of a matrix effect, while the extent of uncertainty is a function of both the matrix effect and the characteristic analyte response.

In summary, these two methods of rapid sample analysis with field-portable XRF systems often achieved the data requirement for screening of ±50% accuracy at and below a concentration of 1000 µg/g. This goal was accomplished for a variety of soil matrices, and the results in Tables 7–9 show that this approach is also promising for several other particulate matrices (e.g., sediment, dust, paint chips, and sludge). The determination of Ni, Co, and Cr, however, was not found to accomplish this goal consistently, even though reported estimates of detection for XRF analysis are well below 1000 µg/g. It appears that for analytes with poor XRF sensitivity, matrix effects are more problematic, and matrixspecific standards would be necessary to achieve a ±50% accuracy.

#### **CONCLUSIONS**

With the exception of Ni, Co, and Cr, the determination of Cu, Zn, As, Pb, Hg, Tl, Se, Ag, Cd, Sn, Sb, and Ba at and below  $1000~\mu g/g$  in a variety of solid particulate materials was often within  $\pm 50\%$  of the expected values when using either funda-

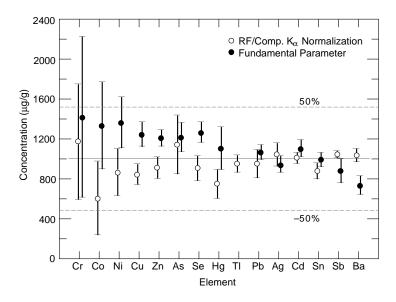


Figure 5. Average and standard deviation of concentrations established for soils spiked with 1000  $\mu$ g metal/g, as determined by RF/Comp.  $K_{\alpha}$  normalization and FP analysis.

mental parameter or response factor/Compton  $K_{\alpha}$  peak-normalization methods of analysis. These alternative approaches to XRF analysis are very useful for screening a variety of matrices during RI/FS activities when it is impractical to produce matrix-matched standards.

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### REPORT DOCUMENTATION PAGE

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